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(58) Field of search

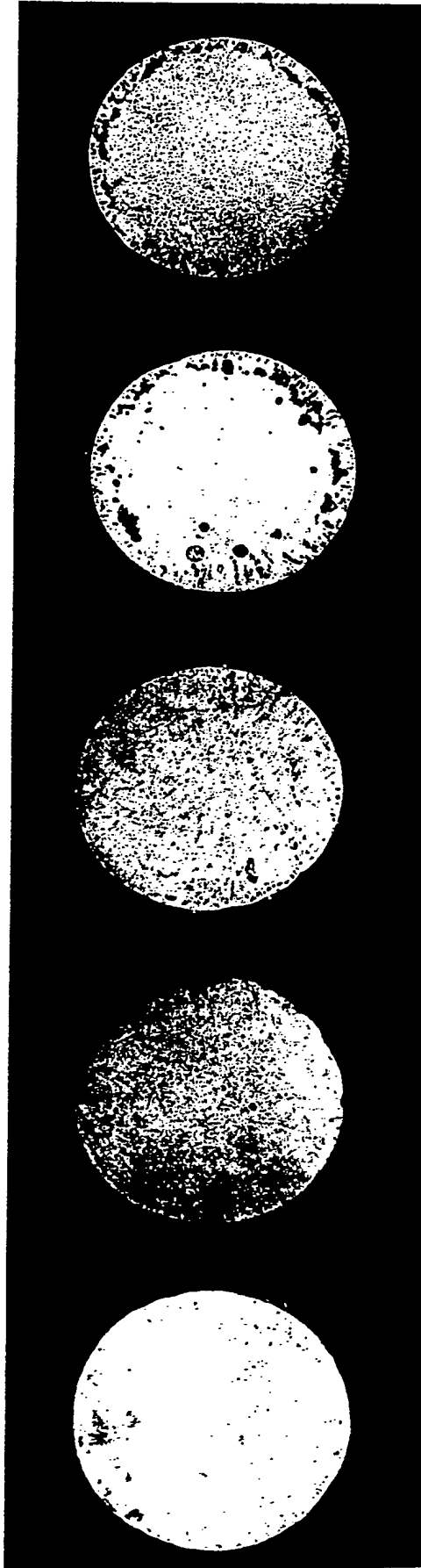
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INT CL<sup>5</sup> B22C  
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(54) **Casting of aluminium-lithium alloys**

(57) Aluminium-lithium alloys show poor suitability as casting materials due to the occurrence of sub-surface porosity in the casting which results from adverse reaction between the molten alloy and the materials used in the manufacture of suitable moulds. In order to prevent this, the mould is first treated with a silylating agent such as trimethylchlorosilane which reacts with free -OH groups in the mould material, thereby passivating the mould surface towards molten lithium. Trial castings made in moulds thus-treated have a much cleaner as-cast surface and show insignificant sub-surface porosity. The silylating agent may be applied by dipping, spraying, or use of a carrier gas, e.g. nitrogen.

**GB 2 262 465 A**

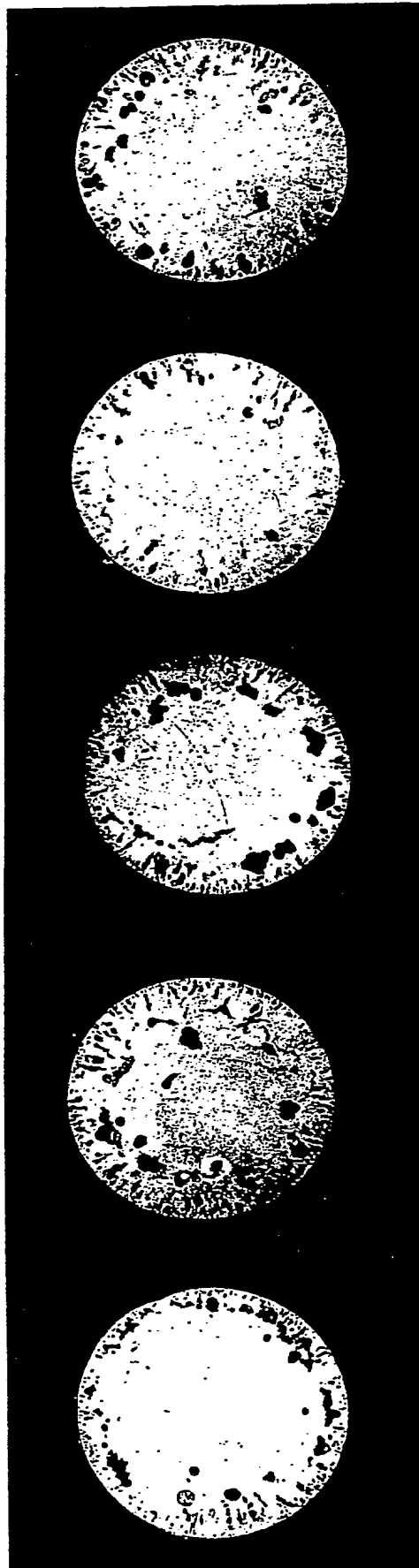
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(a) (b) (c) (d) (e)

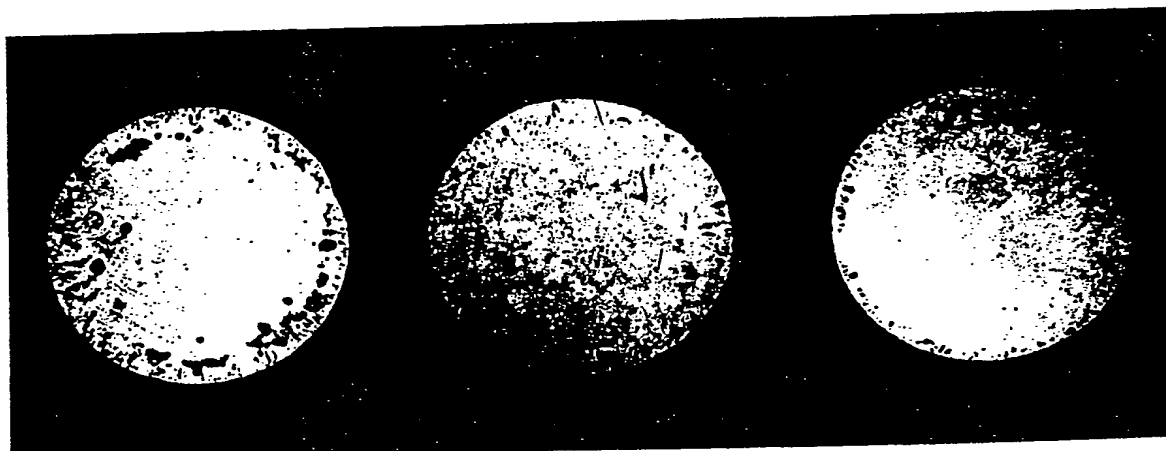
Figure 1

2/5



(a) (b) (c) (d) (e)

Figure 2

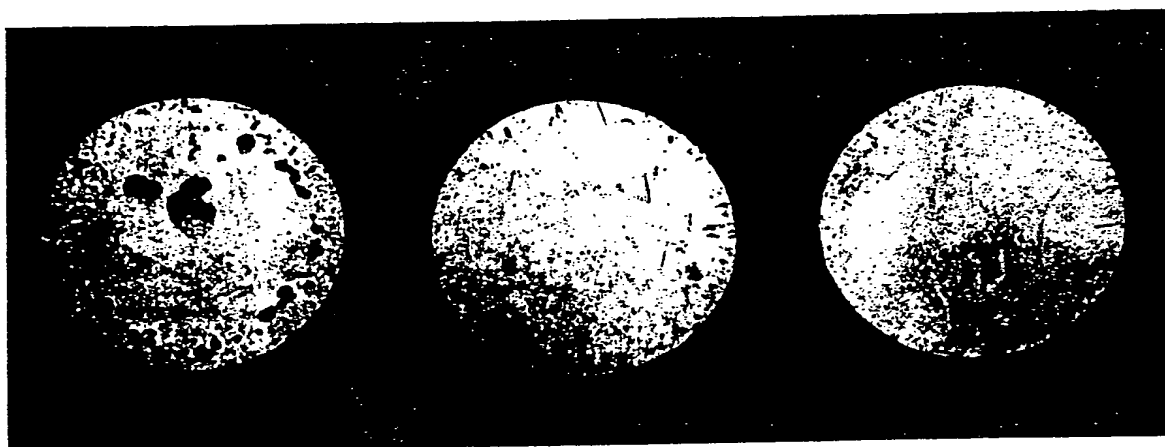


(a)

(b)

(c)

Figure 3



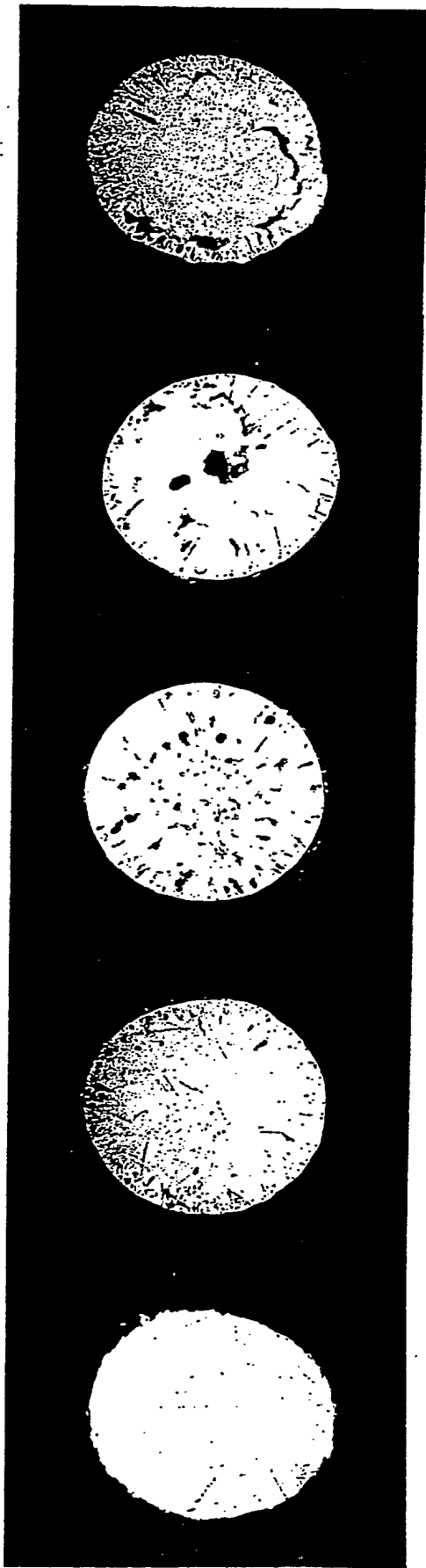
(a)

(b)

(c)

Figure 4

H16



(e)

(d)

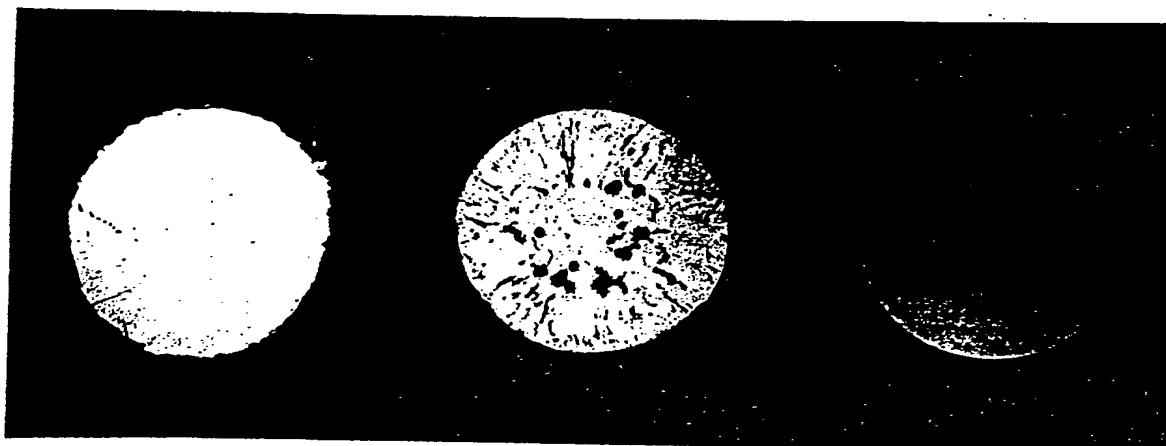
(c)

(b)

(a)

Figure 5

6/5



(a)

(b)

(c)

Figure 6

## CASTING OF ALUMINIUM-LITHIUM ALLOYS

This invention relates to aluminium-lithium alloys containing between 1 and 5% by weight of lithium, and in particular to an improved method of casting such alloys.

During recent years, low density wrought aluminium-lithium alloys have been developed for a variety of aerospace applications. However, these materials are relatively expensive in comparison with conventional non-lithium-containing alloys, so there is a strong incentive to use near net shape production techniques which minimise wastage through scrap. As a result, current research is directed towards the development of an effective casting method for aluminium-lithium alloys. Such a method would enable articles to be produced which are close in form to their intended final shape without excessive wastage.

To date, efforts in this regard have proved unsuccessful for a number of reasons. Firstly, under the conditions required for casting, the aluminium-lithium alloy has a tendency to absorb hydrogen and to lose lithium through oxidation.

The second major problem is that adverse reactions take place between the molten alloy and the materials used to make the mould. These reactions result in an unacceptable degree of porosity at or near the surface of the casting which has proved particularly difficult to prevent.

A recent study of this phenomenon by the inventors has resulted in a better understanding of the underlying causes of the reactions involved. Their investigation has shown that the undesired porosity is caused by the reaction between the lithium constituent of the alloy and the functional groups, especially the -OH groups, found in common mould materials. In certain types of sand mould, for example, these functional groups have been identified as the phenolic -OH terminal groups which arise from the phenolic resin binder after curing.

The binder systems commonly used in sand casting include CO<sub>2</sub>/silicate; ester/silicate; hot box resins; cold box resins; urethane; urea/formaldehyde, and furan-based resins. To a greater or

lesser degree, these systems are all subject to the same kind of adverse reaction with lithium and hence give rise to porosity which it is preferable to avoid.

Similar difficulties arise with investment casting. In this process, the investment mould is made by immersing a pattern fashioned from a standard casting wax in a series of refractory slurries to build up a coating or shell around the pattern. Typically, a primary slurry of zirconium silicate is used for the initial immersions, and this is followed by immersion in a number of back-up slurries which comprise a 70:30 mix of molochite (a type of calcined clay) and zirconium silicate. These back-up slurries are arranged to contain different grades of molochite and are used in order of their particle sizes, finest first. Once the immersion process is complete, the pattern is removed by simply melting the wax and the resulting shell is fired at a temperature of around 900°C.

The degree of porosity in investment castings is less severe than with sand castings. Nevertheless, adverse reactions still occur owing to the presence of inorganic hydroxyl groups which terminate the silicate anions. The effect may also be exacerbated by the presence of adsorbed ethanol and/or water arising from the slurries used to make the investment moulds, since these adsorbed species increase the population of -OH reaction sites. Even though the moulds are fired at temperatures up to 900°C, there may still be sufficient adsorbed material to give rise to a significant degree of hydroxyl activity at the casting interface.

In sand casting, various attempts have been made to reduce the intensity of the adverse reactions by physically coating moulds with a non-reactive lining of alumina applied as a slurry. However, this technique has enjoyed only limited success because there is inevitably some reaction between the molten lithium component and the alumina, albeit on a reduced scale compared with the reaction between molten lithium and phenolic resin binder. There is also some reaction with residual water from the slurry.

It is therefore an aim of this invention to provide a method of casting aluminium-lithium alloys in which reaction between the molten lithium constituent and the mould is reduced to an acceptable level, resulting in negligible surface porosity in the alloy casting.



The invention is a method of casting aluminium-lithium alloys comprising the steps of:

forming a sand or investment mould around a pattern;

5

curing the mould;

treating the cured mould with a silylating agent which reacts with free hydroxyl groups on or near the mould surface to suppress their  
10 reactivity towards molten aluminium-lithium, and

casting the aluminium-lithium alloy in the mould.

Preferably, a silylating agent is used which reacts spontaneously  
15 with the mould surface material at ambient temperature, such as a reagent selected from the group comprising trimethylsilylacetamide, hexamethyldisilazane and especially trimethylchlorosilane.

Conveniently, the silylating agent is a liquid at ambient temperature so that it can be sprayed undiluted onto the mould  
20 surfaces to react *in situ*. In the case of convoluted mould shapes which have surfaces inaccessible to spray application of the silylating agent, a dipping technique may be adopted and excess silylating agent may then be driven off by warming. Alternatively, the silylating agent can be infiltrated into the mould using a dry  
25 carrier gas.

The invention will now be described by way of example with reference to the drawings, in which:

Figure 1 is a photograph showing the variation of porosity with  
30 increasing lithium content for a series of sand-cast aluminium-lithium binary alloys against a reference sample of sand-cast aluminium of 99.9% purity, all prepared using prior art methods;

Figure 2 is a photograph showing the variation of porosity with  
35 increasing binder content in the mould for sand-cast binary aluminium-lithium alloys containing 3% by weight of lithium prepared using prior art methods;

- Figure 3 is a photograph showing the comparison in porosity between a sample cast in an untreated sand mould and two samples cast in sand moulds treated by carrier gas-borne silylating agent;
- Figure 4 is a photograph showing a comparison in porosity between a sample cast in an untreated sand mould and samples cast in sand moulds treated by different methods;
- Figure 5 is a photograph showing the variation of porosity with increasing lithium content for a series of investment-cast aluminium-lithium binary alloys against a reference sample of investment-cast aluminium of 99.9% purity, and
- Figure 6 is a photograph comparing the porosity shown by a drip-treated investment casting, an untreated investment casting and an unalloyed investment casting.

Each of the specimens shown in the Figures was subjected to the same cleaning and polishing steps: After casting, the samples were laterally dissected and one half was mounted in Bakelite (Registered Trade Mark). The mounted sample was then ground using a series of grinding papers of 240, 400, 600 and 1200 grit, respectively, and cleaned using a proprietary detergent such as Decon 90. If necessary, samples were then exposed to ultrasound treatment to dislodge any particles lodged within the defects. Initial polishing was carried out with a 6 micron diamond polishing wheel and, prior to final polishing on a 1 micron diamond polishing disc, the samples were cleaned again with the proprietary detergent.

Referring now to Figure 1, there is shown a series of sand-cast samples 1(a) to (e) which were each cast from the melt into a sand mould containing 1% Alphaset binder and 0.2% TH 8 hardener in proportions by weight. Sample 1(a) is a reference sample of aluminium of 99.9% purity, whilst samples 1(b) to (e) are binary aluminium-lithium alloys containing increasing proportions of lithium from 1 to 4% by weight.

The cleaned and polished surface of reference sample 1(a) shows no sign of porosity, but the binary alloy samples 1(b) to (e) show increasing amounts of porosity in proportion to their increasing lithium content. Sample 1(b) containing only 1% by weight of lithium has a near-smooth surface, whilst sample 1(c) which contains 2% by

weight of lithium has a number of small pores. The sample containing 3% by weight of lithium (1(d)) shows an increase in the amount and severity of sub-surface porosity, whilst sample 1(e) containing 4% by weight of lithium has very deep pores indeed.

5 In practice, commercial aluminium-lithium alloys are likely to have a lithium content somewhere between 2 and 3% by weight, along with other alloying constituents. The trend illustrated in Figure 1 indicates that the proportion of lithium present will have a marked influence on the structural integrity of cast aluminium-lithium  
10 products.

Figure 2 shows a series of binary aluminium-lithium alloys containing 3% by weight of lithium after casting in sand moulds having increasing proportions of the Alphaset phenolic binder. Sample 2(a) cast from a mould containing 1% binder corresponds to sample 1(d) in  
15 Figure 1 above. Sample 2(e) was cast from a mould containing 5% binder and the samples 2(b), (c) and (d) were cast from moulds containing 2, 3 and 4% binder, respectively.

There appears to be no discernible difference between the degree of porosity observed for any of these samples 2(a) to (e). This  
20 indicates that the severity of adverse reaction between the lithium constituent of the alloy and the phenolic binder is independent of binder content at the proportions used in these particular samples and suggests that the critical proportion of binder at which reaction with lithium diminishes to an acceptable level is below the value of 1% by  
25 weight. This is a significant threshold value because the typical level of binder used in a commercial foundry is around 2% by weight.

Turning now to Figure 3, sample 3(a) is a baseline sample of binary aluminium-lithium alloy containing 3% by weight of lithium cast in a mould containing 1% by weight of Alphaset phenolic binder,  
30 corresponding to samples 1(d) and 2(a) above. Samples 3(b) and (c) also contain 3% by weight of lithium, but are cast in a mould containing 2% by weight of binder. These two samples show the improvement which can be achieved by first treating the mould with trimethylchlorosilane (TMCS) as silylating agent using a gassing  
35 technique which is described in more detail below.

In the preparation of gas-borne TMCS-treated moulds, nitrogen is used as a carrier gas to deliver the silylating agent to the mould.

The nitrogen is rigorously dried, firstly by passing it through two tubes of silica gel and then by passage through two tubes of molecular sieve. Meanwhile, the mould to be treated is positioned in a treatment chamber which is totally enclosed except for a gas escape  
5 outlet. The chamber is then flushed with the dry nitrogen in order to displace the air and to remove as much of the moisture as possible, thereby minimising the opportunity for hydrolysis of the TMCS. When flushing is complete, the dry nitrogen stream is diverted through the TMCS at room temperature and this silylating agent is entrained in the  
10 gas stream which passes through the treatment chamber. Treatment typically takes about two hours, after which time the mould is ready to receive the melt.

Ideally, the carrier gas is directed into the mould cavity to ensure that passage of the entrained silylating agent occurs over  
15 every portion of the mould surface which is to form the interface with the casting. As the silylating agent reacts with the free -OH groups of the phenolic binder constituent, hydrogen chloride is given off so it is possible to assess the progress of the treatment by monitoring the concentration of hydrogen chloride in the gases downstream of the  
20 treatment chamber. Treated moulds assume a red colouration on their surfaces.

As clearly seen in Figure 3, the specimens 3(b) and 3(c) have substantially less porosity on their cleaned and polished end faces compared to the untreated specimen 3(a), indicating that the reaction  
25 between the lithium constituent of the alloy and the binder constituent of the mould has been suppressed.

Figure 4 is a photograph of a similar set of samples to those shown in Figure 3, except that sample 4(c) results from casting in a mould which has been treated by dripping undiluted TMCS onto its  
30 surfaces rather than by the gassing technique described above. Sample 4(a) is a baseline sample of binary aluminium-lithium alloy containing 3% by weight of lithium cast in a mould containing 2% by weight of Alphaset phenolic binder, corresponding to sample 2(b) above. Sample 4(b) is the 3% binary aluminium-lithium alloy cast in a mould  
35 containing 2% binder after treatment with nitrogen-borne TMCS shown as sample 3(b) above.

Here it can be seen that sample 4(a) from the untreated mould has

quite severe porosity as would be expected, but sample 4(b) from the gas-treated mould also shows some residual porosity. Sample 4(c) from the drip-treated mould is substantially free of porosity.

The observed difference between drip treatment and gaseous infiltration is thought to be due to non-exposure of the silylating agent to all the available reaction sites. Longer exposure of the mould to the nitrogen-borne TMCS, or alternatively exposure under pressure would be expected to give results for the gassing technique which are at least as good as those obtained with the drip treatment.

10 The photograph of Figure 5 shows a similar series of samples to Figure 1, except that samples 5(a) to (e) were each cast from the melt into an investment shell prepared as follows:

A pattern of standard casting wax was immersed twelve times in a series of coating compositions, firstly three times into a primary  
15 coating composition and then three times each into a series of three back-up coating compositions.

The primary coating composition comprised 200g of zirconium silicate and 40 cm<sup>3</sup> of colloidal silica in water, e.g. Syton (Registered Trade Mark).

20 The back-up coating compositions each comprised a mixture of 70g of molochite with 30g of zirconium silicate and 48 cm<sup>3</sup> of Laksil (Registered Trade Mark) which is ethyl silicate in alcohol. These back-up coating compositions differed from each other only in terms of the grade of molochite employed and were used in order of finest  
25 particle size first, the first back-up coating comprising 120 grade molochite, the second back-up coating comprising 50/80 grade molochite and the third back-up coating comprising 30/80 grade molochite.

In the photograph, sample 5(a) is a reference sample of aluminium of 99.9% purity, whilst samples 5(b) to (e) are binary aluminium-lithium alloys containing increasing proportions of lithium from 1 to  
30 4% by weight. It is clear that there is a marked increase in porosity as the lithium content increases, similar to the effect seen in the sand-cast samples of Figure 1.

In Figure 6 the effect of pre-treatment of the investment shell  
35 can be seen. Here, sample 6(a) corresponds to the reference sample of 99.9% pure aluminium seen at 5(a) above; sample 6(b) is a binary aluminium-lithium alloy containing 3% by weight of lithium similar to

sample 5(d) above, and sample 6(c) is a binary aluminium-lithium alloy containing 3% by weight of lithium which has been cast from an investment shell which has been drip-treated with TMCS.

The reference sample and the TMCS-treated sample are virtually  
5 indistinguishable and porosity-free, whilst the untreated alloy sample shows severe porosity.

Thus it is clear that the method of the present invention provides a means whereby aluminium-lithium alloys may be successfully cast without undesirable porosity which would otherwise undermine the  
10 structural integrity of cast products.

## CLAIMS

1. A method of casting aluminium-lithium alloys comprising the steps of:

forming a sand or investment mould around a pattern;

curing the mould;

treating the cured mould with a silylating agent which reacts with free hydroxyl groups on or near the mould surface to suppress their reactivity towards molten aluminium-lithium, and

casting the aluminium-lithium alloy in the mould.

2. A method of casting aluminium-lithium alloys as claimed in claim 1 wherein the silylating agent is a liquid at ambient temperature which is sprayed undiluted onto the mould surface to react *in situ*.

3. A method of casting aluminium-lithium alloys as claimed in claim 1 wherein the silylating agent is delivered to the mould surface by means of a carrier gas.

4. A method of casting aluminium-lithium alloys as claimed in any preceding claim wherein the silylating agent reacts spontaneously with the mould surface material at ambient temperature and is selected from the group comprising trimethylsilylacetamide, hexamethyldisilazane and trimethylchlorosilane.

**Patents Act 1977**  
**Examiner's report to the Comptroller under**  
**Section 17 (The Search Report)**

Application number

9126620.5

**Relevant Technical fields**

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(ii) Int Cl (Edition 5 ) B22C

Search Examiner

J A WALLIS

**Databases (see over)**

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI

Date of Search

27 JANUARY 1991

Documents considered relevant following a search in respect of claims ALL CLAIMS

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
A	GB 2045789 A (DOW CORNING) whole document pertinent	1
A	DD 291261 A (VEBC) whole document pertinent	1
A	US 4558074 (TORBUS) whole document pertinent	1

SF2(p)

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